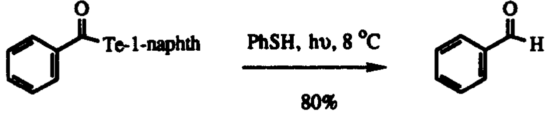
GRAPHICAL ABSTRACTS

Tetrahedron Lett. **1993**, *34*, 1545

THE FREE RADICAL CHEMISTRY OF ACYL TELLURIDES: MECHANISTIC STUDIES AND SYNTHETIC APPLICATIONS

C. Chen and D. Crich,* Dept. of Chemistry, University of Illinois at Chicago (M/C 111), Box 4348, Chicago, Illinois 60680, USA



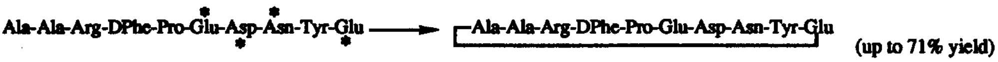
Strong evidence for the formation of acyl radicals in the photolysis of acyl tellurides has been provided by photolysis in the presence of thiophenol. Other mechanistic details of acyl telluride chemistry are addressed and further synthetic applications presented.

Tetrahedron Lett. **1993**, *34*, 1549

A NOVEL, CONVENIENT, THREE-DIMENSIONAL ORTHOGONAL STRATEGY FOR SOLID-PHASE SYNTHESIS OF CYCLIC PEPTIDES.

Steven A. Kates,[a] Nuria A. Solé,[b] Charles R. Johnson,[c] Derek Hudson,[c] George Barany,[b] and Fernando Albericio[a,]*
[a]Millipore Corporation, 75A Wiggins Avenue, Bedford, MA 01730, USA; [b]Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA; [c]Arris Pharmaceutical Corporation, 385 Oyster Point Blvd., South San Francisco, CA 94080, USA

Head-to-tail cyclic peptides are made efficiently by a three-dimensional orthogonal solid phase protection strategy (Fmoc/*t*Bu/allyl), featuring side-chain anchoring to PAC or PAL supports (starting positions indicated by *), selective palladium (0)-catalyzed allyl removal, and resin-bound cyclization mediated by BOP/HOBt/DIEA.

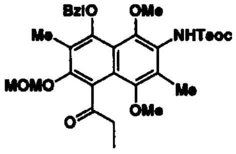

Ala-Ala-Arg-DPhe-Pro-Glu-Asp-Asn-Tyr-Glu ——► Ala-Ala-Arg-DPhe-Pro-Glu-Asp-Asn-Tyr-Glu (up to 71% yield)

Tetrahedron Lett. **1993**, *34*, 1553

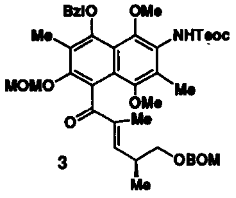
TOWARDS THE SYNTHESIS OF STREPTOVARICIN D: SYNTHESIS OF FULLY ELABORATED AROMATIC PRECURSORS AND COUPLING WITH ANSA CHAIN FRAGMENTS

W. R. Roush* and D. J. Madar, Department of Chemistry
Indiana University, Bloomington, IN 47405

Syntheses of **2**, **3** and **19** (not shown, but with a more fully elaborated ansa chain) are described.



2



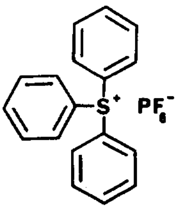
3

Tetrahedron Lett. **1993**, *34*, 1557

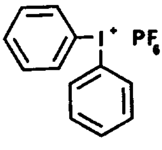
Photochemical Reaction of Onium Salts with N,N-Dimethylaniline: Evidence for Photoinduced Electron Transfer.

Paul F. A. Buijsen and Nigel P. Hacker,*
IBM Research Division, Almaden Research Center,
650 Harry Road, San Jose, California 95120-60299.

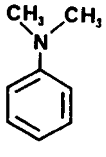
Photolysis of TPS and DPI in the presence of DMA occurs by electron transfer from the singlet excited state of DMA.



TPS



DPI



DMA

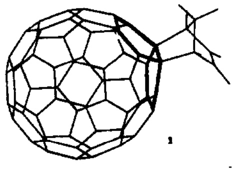
Tetrahedron Lett. **1993,** *34,* 1561

Isolation of Fullerene Products from Flames: Structure and Synthesis of the C60 -Cyclopentadiene Adduct

Vincent M. Rotello,[†*] Jack B. Howard,[‡] Tapesh Yadav,[‡] M. Morgan Conn,[†] Elisabetta Viani,[†] Laura M. Giovane[‡] and Arthur L. Lafleur[§]

[†]Department of Chemistry, [‡] Department of Chemical Engineering, [§]Center for Environmental Health Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139

A C_{60}-C_5H_6 adduct was isolated from a low pressure benzene flame. The structure of this product is identical to the Diels-Alder adduct of C_{60} and cyclopentadiene as established through independent synthesis. This product was determined to be that of adduct 1 through ^{13}C and proton NMR, as well as infrared and mass spectrometry.



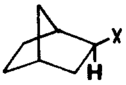
1

Tetrahedron Lett. **1993,** *34,* 1563

The Gamma Gauche Substituent Effect in ^{13}C NMR.

George B. Clemans and Mesfin Alemayehu, Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403 USA and Department of Chemistry, Duke University, Durham, NC 27706 USA

Empirical force field calculations suggest a reason for the variability of the gamma gauche substituent effect and show that they must be interpreted with caution.

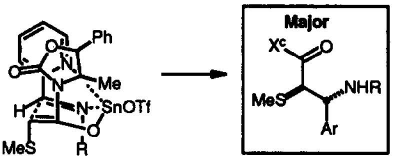


Tetrahedron Lett. **1993,** *34,* 1567

Studies on the Synthesis of Bleomycin A_2: Observations on a Diastereoselective Imine Addition Reaction for C2-Acetamido Side Chain Introduction, Dale L. Boger* and Takeshi Honda

Department of Chemistry, The Scripps Research Institute
10666 North Torrey Pines Road, La Jolla, California 92037 USA

Abstract. A study of the diastereoselective addition of the stannous (Z)-enolates of optically active *N*-acyloxazolidinones with the prototype imine **5** is detailed and provides an approach to the stereocontrolled introduction of the C2-acetamido side chain of the pyrimidoblamic subunit of bleomycin A_2.

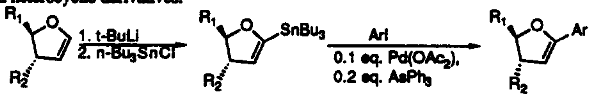


Tetrahedron Lett. **1993,** *34,* 1571

PREPARATION OF 1-(TRI-N-BUTYLSTANNYL) FURANOID GLYCALS AND THEIR USE IN PALLADIUM-MEDIATED COUPLING REACTIONS.

Han-Cheng Zhang, Mohamed Brakta and G. Doyle Daves, Jr.
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180

1-(Tri-n-butylstannyl) furanoid glycals have been prepared and shown to undergo palladium-mediated coupling with iodo aryl and heterocyclic derivatives.

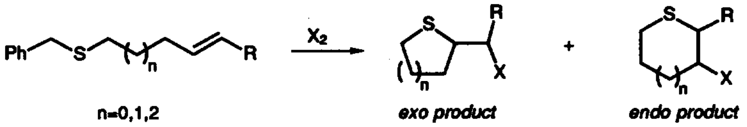


Tetrahedron Lett. **1993**, *34*, 1575

REGIOCHEMICAL STUDIES ON HALOCYCLIZATION REACTIONS OF UNSATURATED SULFIDES

Xiao-Feng Ren and Edward Turos, *Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214 USA*

The regiochemistry for the halocyclizations of olefinic and acetylenic benzylsulfides has been studied.

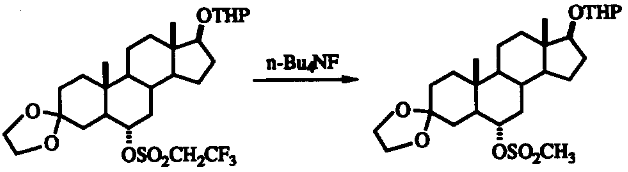


Tetrahedron Lett. **1993**, *34*, 1579

TETRABUTYLAMMONIUM FLUORIDE-INDUCED CONVERSION OF TRESYLATES TO MESYLATES

Yearn Seong Choe and John A. Katzenellenbogen*
Department of Chemistry, University of Illinois, 1209 W. California St., Urbana, IL 61801

Conversion of secondary tresylates to mesylates by tetrabutylammonium fluoride and its proposed mechanism are described.

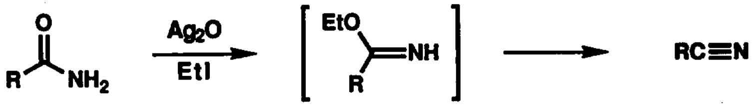


Tetrahedron Lett. **1993**, *34*, 1581

A New Method for the Synthesis of Nitriles from Amides Under Non-Acidic Conditions.

Marcos L. Sznaidman, Curtis Crasto and Sidney M. Hecht*, Departments of Chemistry and Biology, University of Virginia Charlottesville, Virginia 22901

Aryl carboxamides and other electron-rich amides were converted to the respective nitriles in good yields by treatment with Ag_2O and EtI in benzene at reflux.

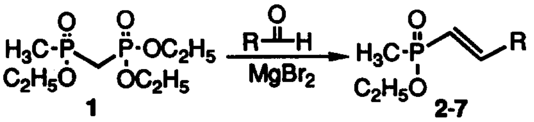


Tetrahedron Lett. **1993**, *34*, 1585

PHOSPHONATE VS. PHOSPHINATE ELIMINATION DURING OLEFINATION OF ALDEHYDES

Mahavir Prashad
Sandoz Research Institute, East Hanover, N.J. 07936, U.S.A.

Olefination of aldehydes with 1 in the presence of magnesium bromide etherate and triethylamine leads to a selective elimination of the phosphonate group to yield alkenyl(methyl) phosphinates (2-7) in a convenient manner.

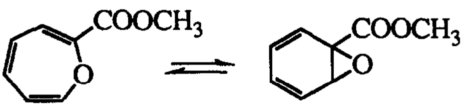


Tetrahedron Lett. **1993**, *34*, 1589

2-CARBOMETHOXYOXEPIN: 1-CARBOMETHOXYBENZENE 1,2-OXIDE. A METABOLITE OF *PHELLINUS TREMULAE*.

William A Ayer* and Elizabete R. Cruz,
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2.

The isolation of 2-carbomethoxyoxepin, a possible biogenetic precursor of methyl salicylate, is described.

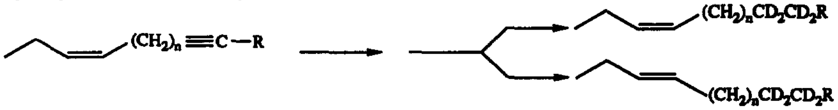


Tetrahedron Lett. **1993**, *34*, 1593

β-Hydroxysilanes in the Synthesis and Labelling of Unsaturated Pheromones.

J. E. Oliver, M. Schwarz, J. A. Klun, W. R. Lusby, and R. M. Waters. ARS/USDA, Beltsville, MD 20705-2350

Olefins can be protected as hydroxysilanes and stereospecifically regenerated after hydrogenation of an acetylene.



Tetrahedron Lett. **1993**, *34*, 1597

REGIOSELECTIVE OPENING OF CHIRAL HYDROXY EPOXIDES: A SHORT ROUTE TO MURICATACIN AND ITS DIASTEREOMER epi-MURICATACIN

Mohamed Saïah, Michel Bessodes* and Kostas Antonakis
Institut de Recherches Scientifiques sur le Cancer, CNRS, 94801-Villejuif Cedex, FRANCE

The dilithioacetate opening of chiral epoxides, obtained by the Sharpless asymmetric epoxidation procedure, led regiospecifically to the corresponding hydroxy γ-lactones thus opening a short route to epi-muricatacin and muricatacin.

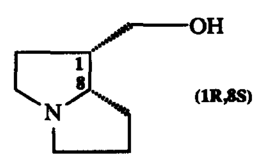
Tetrahedron Lett. **1993**, *34*, 1599

Asymmetric Synthesis with Chiral Hydrogenolysable Amines

A Short Synthesis of (-) Isoretronecanol

G. Haviari, J.P. Célérier, H. Petit, and G. Lhommet*
Université Pierre et Marie Curie. Laboratoire de Chimie des Hétérocycles,
associé au CNRS. 4 Place Jussieu 75252 Paris cedex 05. France

Dihydropyrrole prepared from (S)-α-methylbenzylamine is reduced with high diastereomeric excess. A short route to isoretronecanol is reported



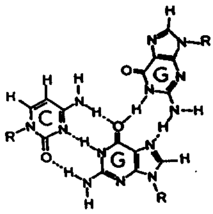
(-) Isoretronecanol

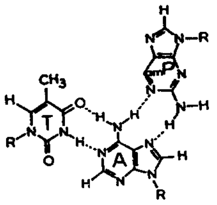
Tetrahedron Lett. **1993**, *34*, 1601

OLIGO-β AND -α-DEOXYRIBONUCLEOTIDES INVOLVING 2-AMINOPURINE AND GUANINE FOR TRIPLE-HELIX FORMATION

Victoria Roig, Robin Kurfurst and Nguyen T. Thuong*
Centre de Biophysique Moléculaire, CNRS, 1A Avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France

Oligo-β and -α-deoxyribonucleotides involving 2-aminopurine (amP) and guanine (G) were synthesized in order to recognize purine sequences in double-helical DNA via isomorphous base triplets amP.AT and G.GC.


G.GC

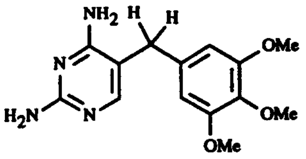

amP.AT

Tetrahedron Lett. **1993**, *34*, 1605

METALATION OF DIAZINES VIII. METALATION OF 4-CHLOROPYRIMIDINE DERIVATIVES. NEW SYNTHESIS OF TRIMETHOPRIM.

Nelly Plé, Alain Turck, Patrice Martin, Sabine Barbey, Guy Quéguiner*
Laboratoire de Chimie Organique Fine et Hétérocyclique ; URA CNRS 1429.
IRCOF-INSA, BP 08, 76131 Mont-Saint-Aignan Cedex. France

A new synthesis of Trimethoprim is described, metalation of a pyrimidine has been used in the key step. An exceptional regioselectivity in the metalation of pyrimidine derivatives as been highlighted.

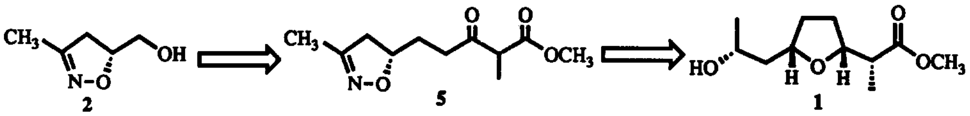

TRIMETHOPRIM

Tetrahedron Lett. **1993**, *34*, 1609

A SHORT AND EFFICIENT SYNTHESIS OF (−)-METHYL 8-*epi*-NONACTATE

Byeang Hyean Kim* and Ju Young Lee, Department of Chemistry, Center for Biofunctional molecules, Pohang Institute of Science and Technology, P.O.Box 125, Pohang 790-600, Korea

The synthesis of the title compound 1 was achieved in seven steps (26% overall yield) from 2.



Tetrahedron Lett. **1993**, *34*, 1611

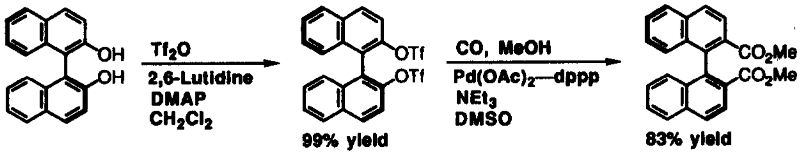
A NEW ENTRY FOR THE CONTROLLED SYNTHESIS OF 2,6-DIDEOXY OLIGOSACCHARIDE.

Kazunobu Toshima*, Yuko Nozaki, Hatsuki Inokuchi, Masaya Nakata, Kuniaki Tatsuta and Mitsuhiro Kinoshita
Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-Ku, Yokohama 223, JAPAN

Tetrahedron Lett. **1993**, *34*, 1615

A Convenient Synthesis of Optically Pure Dimethyl 1,1'-Binaphthalene-2,2'-dicarboxylate from 1,1'-Binaphthalene-2,2'-diol

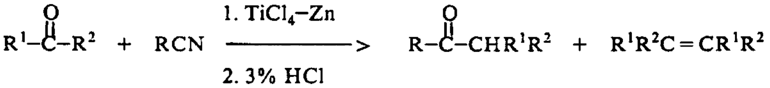
T. Ohta, M. Ito, K. Inagaki and H. Takaya*
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan



Tetrahedron Lett. **1993**, *34*, 1617

Intermolecular Reductive Cross Coupling of Carbonyl Compounds with Nitriles Induced by Low-valent Titanium

Ju Gao, Ming-yang Hu, Jian-xie Chen, Su Yuan, Wei-xing Chen
Department of Chemistry, Nanjing University, Nanjing, 210008, China



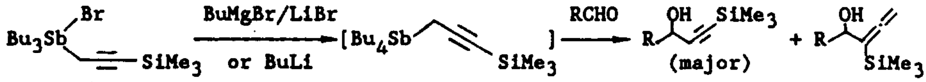
$$R^1-\overset{O}{\overset{\|}{C}}-R^2 + RCN \xrightarrow[2.\ 3\%\ HCl]{1.\ TiCl_4-Zn} R-\overset{O}{\overset{\|}{C}}-CHR^1R^2 + R^1R^2C=CR^1R^2$$

Tetrahedron Lett. **1993**, *34*, 1621

REGIOSELECTIVE REACTIONS OF TRIMETHYLSILYLPROPARGYLIC AND TRIMETHYLSILYLALLYLIC ORGANOANTIMONY COMPOUNDS WITH ALDEHYDES

Li-Jun Zhang, Xue-Sheng Mo, Ji-Ling Huang, Yao-Zeng Huang*
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences

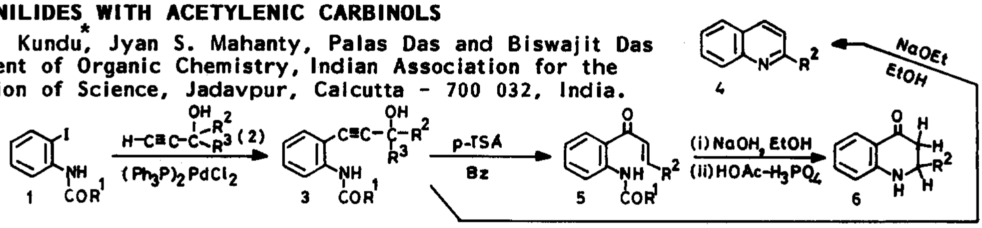
The reactions of trimethylsilylpropargylic organoantimony compound with aldehydes exhibits high acetylene selection in the presence of LiBr.



Tetrahedron Lett. **1993**, *34*, 1625

SYNTHESIS OF QUINOLINES AND 2,3-DIHYDRO-4(1H)-QUINOLONES. PALLADIUM CATALYSED REACTION OF o-IODOANILIDES WITH ACETYLENIC CARBINOLS

Nitya G. Kundu,* Jyan S. Mahanty, Palas Das and Biswajit Das
Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta - 700 032, India.

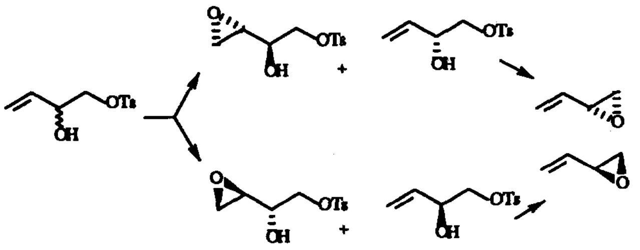


Tetrahedron Lett. **1993,** *34,* 1629

SYNTHESIS OF ENANTIOMERICALLY PURE 3-BUTENE-1,2-DIOL DERIVATIVES VIA A SHARPLESS ASYMMETRIC EPOXIDATION ROUTE.

Constantin Neagu and Tapio Hase*
Department of Chemistry, University of Helsinki, Vuorikatu 20, Helsinki 10, Finland

The six pure chiral C_4 units shown are conveniently accessed by the title reaction.

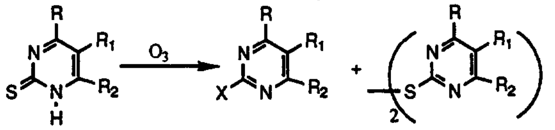


Tetrahedron Lett. **1993,** *34,* 1631

OZONATION OF SUBSTITUTED 2-THIOURACILS AND PYRIMIDINE-2-THIONE.

Claudia Crestini, Raffaele Saladino and Rosario Nicoletti.
Dipartimento di Chimica, Università degli studi di Roma "La Sapienza", p.le Aldo Moro 5, 00100 Italy.

Ozonation of substituted 2-thiouracils and pyrimidine-2-thione is reported.



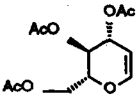
X= H, OH, OR'

Tetrahedron Lett. **1993,** *34,* 1635

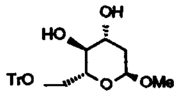
STRAIGHTFORWARD HOMOCHIRAL SYNTHESIS OF THE LACTONE MOIETY OF MEVINIC ACIDS

Christopher J. France, Ian M. McFarlane, Christopher G. Newton*, Philippe Pitchen*, Michael Webster
Rhône-Poulenc Rorer Ltd., Dagenham Research Centre, Rainham Road South, Dagenham, ESSEX RM10 7XS, UK

The key, diastereoselective O-glycosidation of 2 is described, which followed by methanolysis and tritylation gives a simple and efficient one-pot process for the preparation of 5, a key synthon in the preparation of mevinic acids.



2

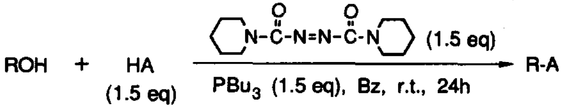


5

Tetrahedron Lett. **1993,** *34,* 1639

1,1'-(AZODICARBONYL)DIPIPERIDINE-TRIBUTYLPHOSPHINE, A NEW REAGENT SYSTEM FOR MITSUNOBU REACTION.

Tetsuto Tsunoda,* Yoshiko Yamamiya, and Shô Itô
Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Tokushima 770, Japan



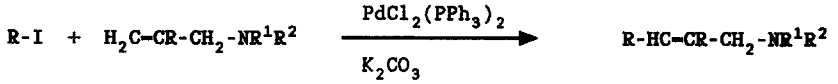
R = Bu, Bn, Crotyl, etc.
HA = TsNHMe, $CH_2(CO_2Et)_2$, $CF_3CONHBn$

The system activates nitrogen or carbon nucleophiles, known to be innert or poorly reactive with the Mitsunobu reagent, to react with primary alcohols satisfactorily forming C-N or C-C bonds.

Tetrahedron Lett. **1993**, *34*, 1643

PALLADIUM-CATALYZED COUPLING OF ORGANIC HALIDES AND TERTIARY ALLYLIC AMINES

L.Filippini; M.Gusmeroli; R.Riva
Isagro, Via Fauser 4, Novara, Italy



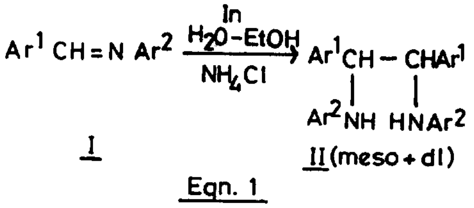
$$R\text{-}I + H_2C{=}CR\text{-}CH_2\text{-}NR^1R^2 \xrightarrow[K_2CO_3]{PdCl_2(PPh_3)_2} R\text{-}HC{=}CR\text{-}CH_2\text{-}NR^1R^2$$

$R = Ar,\ C_nF_{2n+1}$

Tetrahedron Lett. **1993**, *34*, 1647

Novel Reductive Coupling of Aldimines by Indium Under Aqueous Conditions

N.Kalyanam*and G. Venkateswara Rao
R & D Centre, Pharma Division, SPIC Ltd.,
Maraimalai Nagar,Tamil Nadu, 603 209,
INDIA

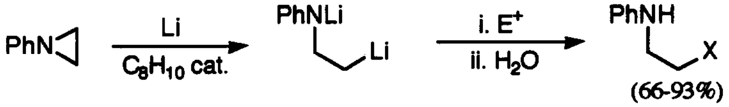


Eqn. 1

Tetrahedron Lett. **1993**, *34*, 1649

NAPHTHALENE-CATALYSED REDUCTIVE OPENING OF AZIRIDINES WITH LITHIUM: A DIRECT PREPARATION OF *N*-LITHIO-2-LITHIOALKYLAMINES

J. Almena, F. Foubelo and M. Yus*
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

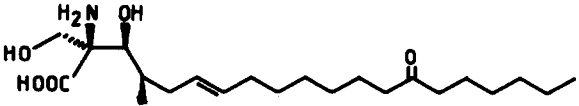


$[E^+ = H_2O, D_2O, Me_2S_2, Bu^tCHO, (CH_2)_5CO]$

Tetrahedron Lett. **1993**, *34*, 1653

A FORMAL SYNTHESIS OF A NOVEL IMMUNOSUPPRESSANT ISP-1 : STEREOCONTROLLED Pd(O) CATALYSED cis-HYDROXYAMINATION OF CARBOHYDRATE DERIVED VINYL EPOXIDE.

A V Rama Rao*, Mukund K Gurjar, T Rama Devi and K Ravi Kumar
Indian Institute of Chemical Technology, Hyderabad 500 007, India

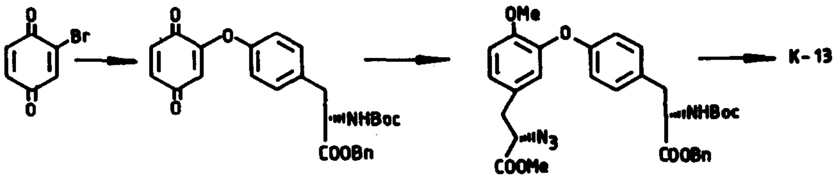


ISP-1

Tetrahedron Lett. **1993**, *34*, 1657

A NEW ROUTE TO ISODITYROSINE-DERIVED CYCLIC PEPTIDES : APPLICATION TO K-13

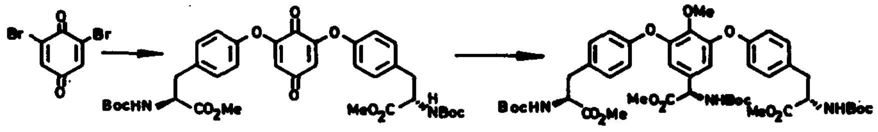
A V Rama Rao*, Mukund K Gurjar, A Bhaskar Reddy and Vivek B Khare
Indian Institute of Chemical Technology, Hyderabad 500 007, India



Tetrahedron Lett. **1993**, *34*, 1661

AN EXPEDIENT APPROACH TO THE DIPHENYL ETHER CROSS-LINKED AMINO ACIDS OF GLYCOPEPTIDE ANTIBIOTICS

A V Rama Rao*, Mukund K Gurjar, Vijay Kaiwar and Vivek B Khare
Indian Institute of Chemical Technology, Hyderabad 500 007, India

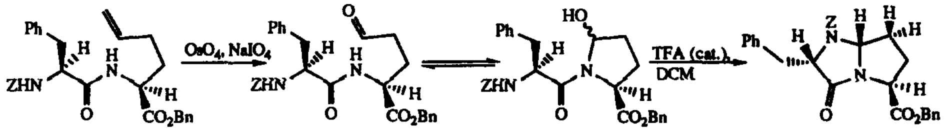


Tetrahedron Lett. **1993**, *34*, 1665

SYNTHESIS OF A BICYCLIC γ-LACTAM DIPEPTIDE ANALOGUE

Jack E. Baldwin[a], Christopher Hulme[a], Alison J. Edwards[a], Kevin E. B. Parkes[b], and Christopher J. Schofield[a].
[a] The Dyson Perrins Laboratory and the Oxford Centre for Molecular Sciences, South Parks Road, Oxford, OX1 3QY, U.K. [b]. Roche Products Limited, PO Box 8, Welwyn Garden City, Herts, AL7 3AY, U.K.

The synthesis of a novel conformationally restrained dipeptide analogue, involving a diastereoselective bicyclisation reaction is described.

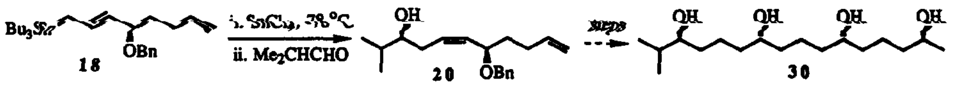


Tetrahedron Lett. **1993**, *34*, 1669

STEREOSELECTIVE SYNTHESIS OF ALIPHATIC 1,5,9,13-POLYOLS USING (δ-ALKOXYALLYL)STANNANES

A.H. McNeill and E.J.Thomas*,
Department of Chemistry, University of Manchester, Manchester, M13 9PL, U.K.

Aliphatic 1,5,9,13-polyols, e.g. 30, are prepared stereoselectively using tin(IV)chloride mediated reactions between aldehydes and the 4-benzyloxyocta-2,7-dienylstannane 18.

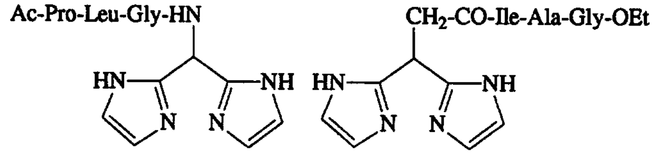


Tetrahedron Lett. **1993**, *34*, 1673

SYNTHESIS OF PEPTIDES CONTAINING BIS-IMIDAZOLE LIGANDS

Zs. Likó and H. Süli-Vargha*
Research Group of Peptide Chemistry, Hung. Acad. Sci.
H-1518 Budapest 112, P.O. Box 32, Hungary

Synthesis of bis-imidazolyl derivatives of the two fragments of the vertebrate collagenase enzyme specific sequence (-Pro-Leu-Gly-Ile-Ala-Gly-) is described.



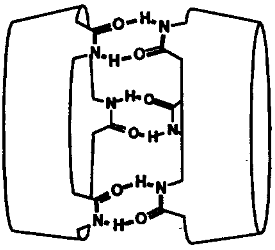
Tetrahedron Lett. **1993**, *34*, 1677

SELF-ASSOCIATING CYCLOCHOLATES

Richard P. Bonar-Law* and Jeremy K. M. Sanders

Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

Self-complementary steroidal triamides have been prepared and their reversible self-assembly into molecular cylinders demonstrated.



Tetrahedron Lett. **1993**, *34*, 1681

CADMIUM CHLORIDE-MAGNESIUM-WATER : A NEW SYSTEM FOR REDUCTION OF VARIOUS ORGANIC FUNCTIONALITIES

Manobjyoti Bordoloi, Natural Products Chemistry Division, Regional Research Laboratory, Jorhat-785 006, Assam, INDIA.

Cadmium chloride-magnesium-water efficiently reduced aldehyde and ketones to their corresponding alcohols, epoxide to mono-alcohol, benzyl halide to toluene, acid chloride to aldehyde and hydrolyzed thioketal to corresponding ketones.